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CALCULATION OF THE PROPERTIES OF TWO-COMPONENT BORATE GLASSES CONTAINING MODIFIER OXIDES FROM THE FIRST AND SECOND GROUPS OF THE PERIODIC TABLE

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Equations are proposed for calculating the concentrations of structural groups with constant composition (SGC) in borate glasses, containing modifier oxides from the first and second groups of the periodic table. The partial molar volumes of SGC are determined and the molar volume of glasses from the systems indicated is calculated using the additive approximation formula. The computed values of V_m satisfactorily approximate the experimental data obtained by different authors — the maximum standard computational error does not exceed 2.5%.

Raman scattering (RS) spectroscopy studies of the structure of sodium and barium borate glasses have established that structural groups with constant composition (SGC) corresponding to the molecular formula B_2O_3 and Na and Ba tetra-, di-, and metaborates are present in these glasses [1–3]. The data obtained on the SGC concentration in the glasses studied by analyzing the RS spectra were used in these works to calculate a number of properties of glasses, for example, the molar volume, using the additive approximation formula

$$Y = \Sigma y_i I_i, \quad (1)$$

where Y is the property whose value is being computed, y_i are the partial coefficients of the SGC, and I_i is the content of SGC in the glass (molar fractions).

In the present article the possibility of approximating the concentration dependences of the properties of the glasses using the relation (1) and the values of I_i obtained computationally and not from data obtained by direct measurements, for example, by a spectral method, is checked.

The equations for calculating the SGC concentration I in glasses with different modifier oxide content x were obtained by a linear approximation on the basis of the following considerations.

Only SGC with the molecular formula B_2O_3, i.e., $I_1^{B_2O_3} = 1$ with $x_1 = 0$, are present in glassy boron anhydride. When a modifier oxide is added, the least important SGC with the chemical formula for a tetraborate starts to form, as a result of which $I_1^{B_2O_3}$ decreases systematically, reaching the value $I_1^{B_2O_3} = 0$ for $x_2 = 0.2$, which corresponds to the modifier oxide content in tetraborate. Therefore, for tetraborate with $x_1 = 0$ $I_1^{R.4B} = 0$ (R is the modifier oxide cation and B is B_2O_3), and for $x_2 = 0$ $I_1^{R.4B} = 1$ The boundary values of x_i and I_i for SGC formed with $x > 0.2$ can be determined analogously. The initial data and the equations obtained for calculating the SGC are presented in Table 1, and the concentration dependences of the computed values of I_i for different SGC are presented in Fig. 1. As Fig. 1 shows, the computed values of I_i satisfactorily fit the experimental data obtained in, for example, [3] for barium-borate glasses.

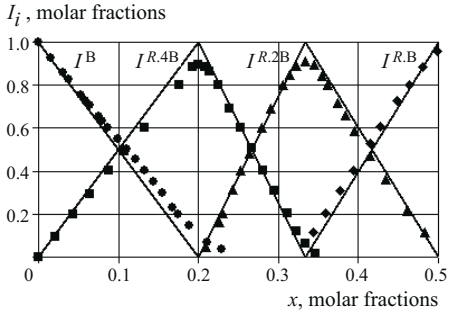

Fig. 1. SGC concentrations I_i versus the composition of $R_2O - B_2O_3$ and $RO - B_2O_3$ glasses. Lines) computed values of I_i; dots) experimental values of I_i obtained by computer digitization of the data from [3].

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Subsequent calculations established the partial coefficients of SGC which appear in the relation (1), specifically, the values of the partial molar volumes v_{mi} of the structural groups present in those two-component glasses in the systems $R_2O - B_2O_3$ and $RO - B_2O_3$ for which data on the density have been published in the literature. Sources which give the analytical compositions of glasses synthesized in platinum crucibles were chosen for the calculations.

The calculation was performed by the least-squares method using the relation (1), which in the present case had the form

$$V_{mi} = \Sigma v_{mi} I_i , \qquad (2)$$

where V_{mi} are the experimental values of the molar volumes of the glasses in the series analyzed (in cm^3/mole); v_{mi} are the partial coefficients of SGC (cm^3/mole); and, I_i are the computed values of the SGC content in the glass, molar fractions, determined using the appropriate equations presented in Table 1.

The partial molar volumes determined for SGC are presented in Table 2. The molar volume V_{mi}^{B} of the glassy boron anhydride was taken to be 37.88 cm^3/mole on the basis of its average density 1.838 g/cm^3 [4].

According to the data in Table 2, the computed values of the partial molar volumes of SGC (V_{mi}^{SGC}), as a rule, have lower values than in glassy B_2O_3 (the only exception is the "largest" cation — Cs^+), in connection with which the introduction of modifier oxides into borate glasses is ordinarily accompanied by a decrease of their V_m, i.e., by an increase of the compactness of the glass-forming network.

A definite correlation is observed between the values of the partial molar volumes of SGC (V_{mi}^{SGC}) and the cube of the radius r of the cation in modifier oxides: V_{mi} increases nearly linearly as r^3 increases (Fig. 2). Correspondingly, the compacting effect of the modifier oxides on the glass-forming network of borate glasses becomes weaker with increasing r, especially in the series of alkali-borate glasses (see Fig. 2*a*).

The computed values obtained for the molar volume of borate glasses using the relation (1) and the established partial coefficients of SGC (V_{mi}^{SGC}) satisfactorily fit the experimental data (Figs. 3 and 4). The relative standard errors ΔV_m in the calculation of the molar volume of two-component

TABLE 1.

SGC	Molecular formula of SGC*	Interval of values of I, molar fractions		Interval of values of x, molar fractions		Working equation
		I_1	I_2	x_1	x_2	
B_2O_3	B_2O_3	1	0	0	0.2000	$I = 1 - 5x$
Tetraborate	$R_2O \cdot 4B_2O_3$	0	1	0	0.2000	$I = 5x$
		1	0	0.2000	0.3333	$I = 2.5 - 7.5x$
Diborate	$R_2O \cdot 2B_2O_3$	0	1	0.2000	0.3333	$I = 7.5x - 1.5$
		1	0	0.3333	0.5000	$I = 3 - 6x$
Metaborate	$R_2O \cdot B_2O_3$	0	1	0.3333	0.5000	$I = 6x - 2$

* The molecular formulas of SGC containing RO have a similar form.

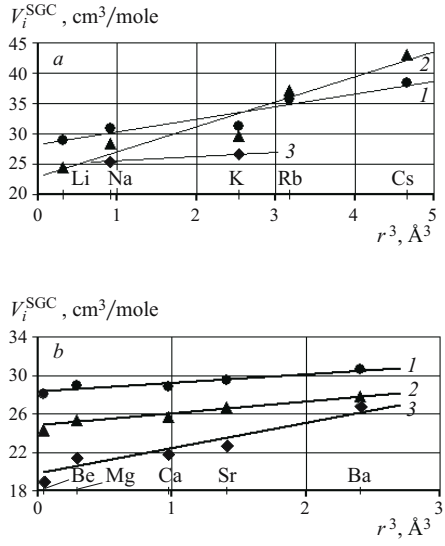

Fig. 2. Molar volume of SGC of $R_2O - B_2O_3$ (*a*) and $RO - B_2O_3$ (*b*) glasses versus the cube of the cation radius r of the modifier oxide [r) data of [5]]. V_i^{SGC}) tetraborate (*1*), diborate (*2*), and metaborate (*3*) of the corresponding cations; ●, ▲, and ■) values obtained for V_i^{SGC} of Be by extrapolation.

TABLE 2.

System	Computed* partial molar volumes of SGC, cm^3/mole			Number of glass compositions
	$V_m^{R.4B}$	$V_m^{R.2B}$	$V_m^{R.B}$	
$Li_2O - B_2O_3$	28.95	24.43	Not determined**	22
$Na_2O - B_2O_3$	30.86	28.36	25.44	32
$K_2O - B_2O_3$	31.31	29.60	26.55	32
$Rb_2O - B_2O_3$	35.73	37.08	Not determined**	20
$Cs_2O - B_2O_3$	38.41	43.10	Same	19
$BeO - B_2O_3$***	28.05	24.32	18.90	1
$MgO - B_2O_3$	28.92	25.34	21.38	4
$CaO - B_2O_3$	28.86	25.69	21.74	12
$SrO - B_2O_3$	29.54	26.62	22.64	21
$BaO - B_2O_3$	30.65	27.80	26.77	36

* The initial values of the glass densities are taken from [4].

** No data on glasses where the molar content of the modifier oxide exceeds 33.33% are given in the sources used.

*** The values of I_i^{SGC} for beryllium-borate glasses were obtained by extrapolation (see Fig. 2*b*).

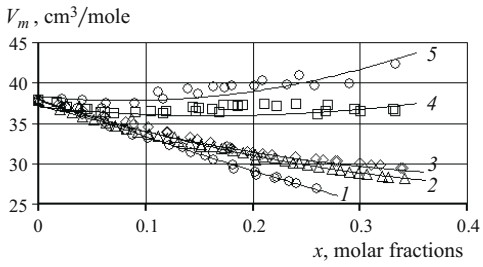

Fig. 3. Concentration dependences of the molar volume of $R_2O - B_2O_3$, R – Li (*1*), Na (*2*), K (*3*), Rb (*4*), and Cs (*5*) glasses. Curves) computed values; dots) experimental values (data obtained by different authors, see Table 2).

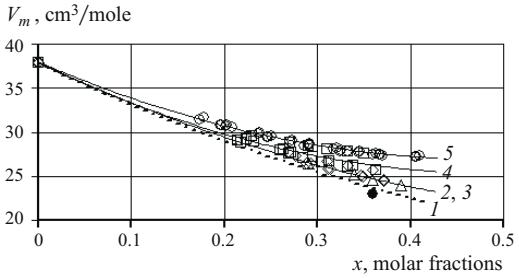

Fig. 4. Concentration dependences of the molar volume of $R_2O - B_2O_3$, R – Be (*1*), Mg (*2*), Ca (*3*), Sr (*4*), and Ba (*5*) glasses. Curves) computed values; dots) experimental values (data obtained by different authors, see Table 2); *1*) computed values obtained by extrapolation.

glasses in the systems $R_2O - B_2O_3$ and $RO - B_2O_3$ using the additive approximation formula and the partial molar volumes established for SGC in the present work are presented in Table 3.

In summary, the computed values of the concentrations of the structural groups of constants composition I_i^{SGC} in two-component alkali- and alkali-earth-borate glasses with modifier oxides from the first and second groups of the periodic table (Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O and BeO, MgO, CaO, BaO), obtained by the equations proposed, agree with the experimental values of I_i^{SGC} determined by direct measurements, for example, from the RS spectra.

The partial molar volumes of SGC were determined and used to calculate the molar volume of the glasses in the above-indicated systems using the additive approximation formula. The computational results satisfactorily fit the experimental values obtained by different authors — the maximum standard computational error in V_m does not exceed 2.5%.

TABLE 3.

System	ΔV_m, %	Number of glass compositions	
		from analysis	from synthesis
$Li_2O - B_2O_3$	0.66	22	None
$Na_2O - B_2O_3$	1.17	32	″
$K_2O - B_2O_3$	1.87	17	15
$Rb_2O - B_2O_3$	2.13	None	20
$Cs_2O - B_2O_3$	2.39	″	19
$BeO - B_2O_3$	–	″	1
$MgO - B_2O_3$	0.16	″	4
$CaO - B_2O_3$	1.76	8	4
$SrO - B_2O_3$	2.17	15	6
$BaO - B_2O_3$	0.45	36	None

The data obtained show that the collection of SGC in various alkali-borate and alkaline-earth-borate glasses can be regarded as identical, including SGC corresponding to the molecular formula B_2O_3, tetra-, di-, and metaborates of the corresponding cations of the modifier oxides.

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